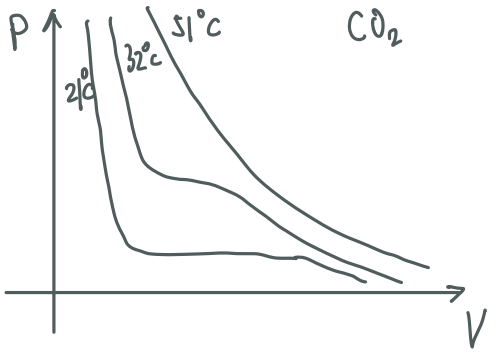
Van der Waals interactions

Strong bonds: ionic bond, covalent bond, metallic bond, hydrogen bond & vdW forces

VdW: Distance-dependent interations between molecules or atoms.

- Liquefaction of gas (Andrew 1869)



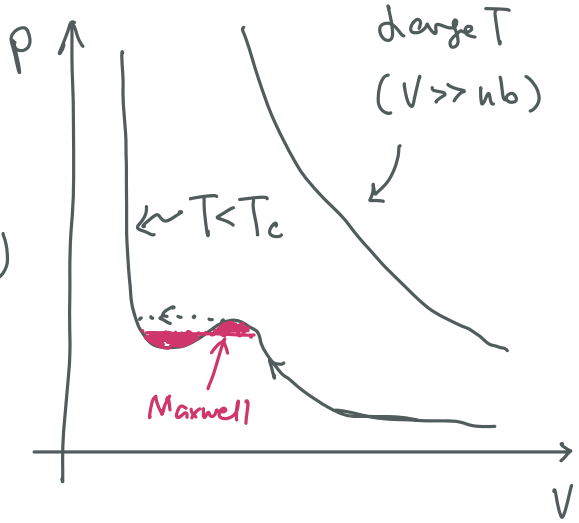
The existence of critical temperature and critical pressure for the phase change

- VDW equation of state (1873, Nobel price 1910)

$$PV = nRT \quad \text{(ideal gas law)}$$

$$\downarrow$$

$$\left(P + \frac{n^2 a}{V}\right)(V - nb) = nRT \quad \text{(Real gas law)}$$



n - number of moles

b - volome of a mole of particles

a - measure of average attraction between particles

Keesom Theory (1921): Forces between permanent dipoles 永久偶极子.

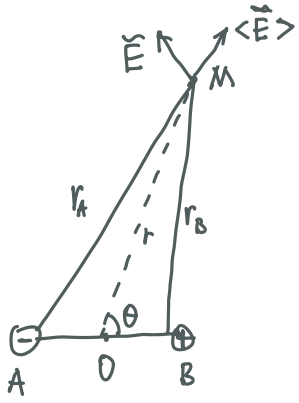
- Potential of a charge

$$V(\vec{r}) = \frac{q}{4\pi\varepsilon r} \qquad r = |\vec{r}|.$$

↑ Permittivity 介电常数.

- Potential of a dipole

Dipole: A combination of two opposite electric charges $+q$ & $-q$ set apart by a small l. $\vec{\mu} = q\vec{l}$ is dipolar moment. ($l \sim 0.1$ nm)



$$V = \frac{q}{4\pi\varepsilon_0}\left(-\frac{1}{r_A} + \frac{1}{r_B}\right)$$

$$r_{A,B} = \left(\frac{l^2}{4} + r^2 \pm lr\cos\theta\right)^{1/2}$$

$$= r\left(1 \pm \frac{l}{r}\cos\theta + \frac{l^2}{4r^2}\right)^{1/2}$$

$$\simeq r\left[1 \pm \frac{l}{2r}\cos\theta + O\left(\frac{l}{r}\right)^2\right]$$

$$V \simeq \frac{q}{4\pi\varepsilon_0 r}\left(\frac{1}{1 - \frac{l}{2r}\cos\theta} - \frac{1}{1 + \frac{l}{2r}\cos\theta}\right) = \frac{ql}{4\pi\varepsilon_0 r^2}\cos\theta$$

The field $\vec{E}$ at point M caused by dipole AB of μ is $-\nabla V$:

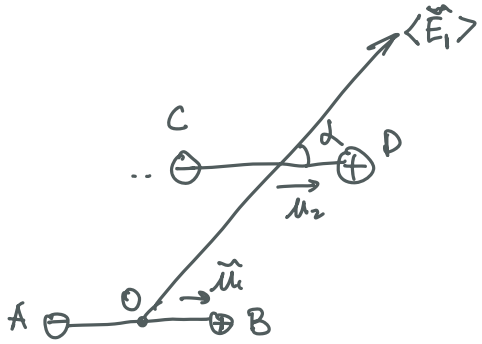
$$E_r = -\frac{\partial V}{\partial r} = \frac{\mu}{2\pi\varepsilon_0 r^3}\cos\theta, \qquad E_\theta = -\frac{1}{r}\frac{\partial V}{\partial \theta} = \frac{\mu}{4\pi\varepsilon_0 r^3}\sin\theta$$

$$\rightarrow E = |\tilde{E}| = \sqrt{E_r^2 + E_\theta^2} = \frac{\mu}{4\pi\varepsilon_0 r^3}\sqrt{1+3\cos^2\theta}$$

If the dipole is free to rotate. with equal probability, there is a mean field ALONG $\overrightarrow{OM}$:

$$\langle \cos^2\theta \rangle = \frac{\int_0^{2\pi} d\phi \int_0^{\pi} \cos^2\theta \sin\theta \, d\theta}{\underbrace{\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta}_{=4\pi}} = \frac{1}{3} \rightarrow \boxed{\langle E \rangle = \frac{\sqrt{2}\mu}{4\pi\varepsilon_0 r^3}}$$

- Dipole in an electric field.



Potential energy $U = -\tilde{\mu}_2 \langle \tilde{E}_1 \rangle = -\mu_2 \langle E_1 \rangle \cos\alpha$

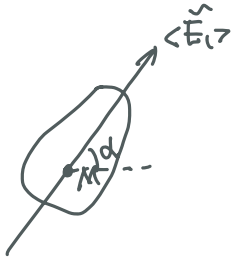
Dipole - Dipole interation $U \sim \frac{\mu_1 \mu_2}{\varepsilon_0 r^3}$

$\mu \sim 1.6\times10^{-19}\,C \times 0.1\,nm$. $\varepsilon_0 \sim 8.854\times10^{-12}\,C^2/(Jm)$. $k \sim 1.38\times10^{-25}\,J/K$. $T \sim 300\,K$

$$\boxed{\frac{U}{kT} \sim \left(\frac{0.36\,nm}{r}\right)^3 << 1 \quad \text{as } r \gtrsim 1\,nm}$$

With thermal energy, both dipoles can rotate "freely" $\rightarrow \langle \cos\alpha \rangle = 0$?

Angle-averaged potential is not ZERO cause' there is always Boltzmann Weighting factor that gives weight to orientations that have a lower energy.



$$P(\alpha) \propto \exp\left[-U(\alpha)/kT\right] = Ae^{z\cos\alpha}, \quad z = \frac{\mu_2 \langle E_1 \rangle}{kT} << 1$$

so that $\int Ae^{z\cos\alpha}\, d\Omega = 1$, $d\Omega = d\theta \sin\alpha \, d\alpha = 2\pi \int_{\pi}^{0} d(\cos\alpha)$

$$\langle U \rangle = -\int d\Omega \; p(\alpha)\, \mu_2 \langle E_1 \rangle \cos\alpha$$

$$= -\mu_2 \langle E_1 \rangle \frac{2\pi \int_0^{\pi} e^{z\cos\alpha} \cos\alpha \, d(\cos\alpha)}{2\pi \int_0^{\pi} e^{z\cos\alpha} \, d(\cos\alpha)}$$

(denominator: $\int_0^{\pi} e^{z\cos\alpha} \, d(\cos\alpha)$ ← $1/A$)

Let $x = \cos\alpha$, Let $I = \int_{-1}^{1} e^{zx} dx = \frac{2\sinh z}{z}$

$$= -\mu_2 \langle E_1 \rangle \frac{\int_{-1}^{1} x e^{zx} dx}{\int_{-1}^{1} e^{zx} dx} = \mu_2 \langle E_1 \rangle \frac{1}{I} \frac{dI}{dz}$$

$$= -\mu_2 \langle E_1 \rangle \left(\coth z - \frac{1}{z} \right)$$

(coth: Hyperbolic cotangent 双曲余切; $\coth z - \frac{1}{z}$ ← Langevin's function)

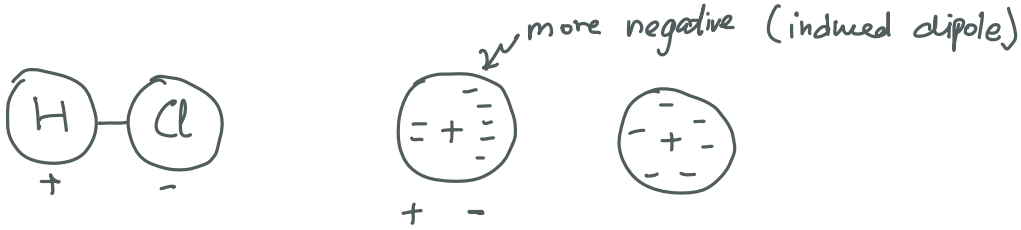
$$\coth = \frac{1}{z} + \frac{z}{3} - \frac{z^3}{45} + \frac{2z^5}{945} + O(z^7) \quad (\text{Note } z \ll 1)$$

$$\Rightarrow \boxed{\langle U \rangle = -\frac{1}{3} \mu_2 \langle E_1 \rangle z = -\frac{1}{3} \frac{\mu_2^2 \langle E_1 \rangle^2}{kT} = -\frac{1}{(4\pi\varepsilon_0)^2} \frac{2\mu_1^2 \mu_2^2}{3kT} \frac{1}{r^6}}$$

Correction is needed to describe the influence of $\vec{\mu}_2$ on the orientation probability of dipole 1 ("slightly" longer)

Keesom's theory gives a force law r^{-7}, of the proper order of magnitude. However, numerical values from μ_1, μ_2 and variation with T do NOT agree with Experiments, showing that vdW is almost T-independent.

The Debye Theory (1920): Dipole-induced dipole interaction



In an electric field E, a molecule takes an induced dipolar moment

$$\mu_{in} = \alpha_0 E$$

by deformation of electronic cloud, $\alpha_0 \propto V \times 4\pi\varepsilon_0$

$$U = -\alpha_{02}\langle E_1\rangle \times \langle E_1\rangle - \alpha_{01}\langle E_2\rangle \times \langle E_2\rangle$$

$$= -\frac{1}{(4\pi\varepsilon_0)^2}\frac{\alpha_{02}\mu_1^2 + \alpha_{01}\mu_2^2}{r^6}$$

However, such induced forces are too weak!

The London Theory (1930): disperson force. Instanteous dipole - induced dipole interation

Attraction forces come from the coupling of oscillations of two neighbouring molecules vibriating in resonance, explaining the cohesion of liquid, solid or rare gases whose atoms are spherical with no permanent dipolar moment.

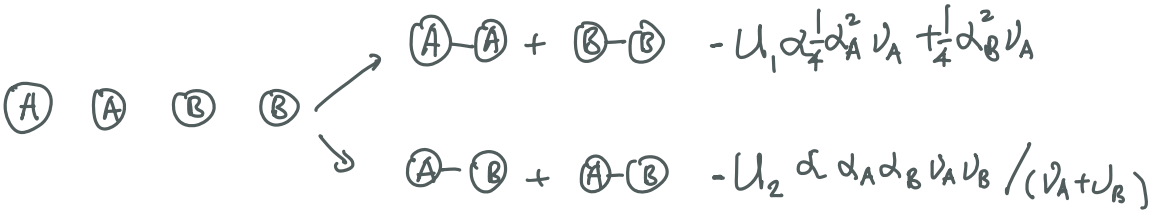
- $U = \frac{-1}{(4\pi\varepsilon_0)^2}\frac{3\alpha^2 h\nu_0}{4}\frac{1}{r^6}$ for two molecules

(α: Polarizability, h: Planck constant, ν_0: electronic absorption frequency)

Molar weight	Molecules	Boiling point	Electrons.
38	F_2 (g)	−188°C	$9e^-$
70.9	Cl_2 (g)	−34°C	$17e^-$
159.8	Br_2 (l)	59°C	$35e^-$
253.8	I_2 (s)	114°C	$53e^-$

Eg. CH_4 (16) vs. $CH_3CH_2CH_2CH_3$ (C_4H_{10}, 58)?

- $U = -\underbrace{\frac{1}{(4\pi\varepsilon_0)^2}\frac{3\alpha_A\alpha_B h\nu_A\nu_B}{2(\nu_A+\nu_B)}}_{\text{London constant.} \sim 10^{-79}\ J m^6}\frac{1}{r^6}$ for two dissimilar molecules



$$\Delta U = U_2 - U_1 \propto \frac{\alpha_B^2\nu_B^2}{\nu_A+\nu_B}\left[\left(\frac{\alpha_A\nu_A}{\alpha_B\nu_B}-1\right)^2 + \frac{\nu_A}{\nu_B}\left(\frac{\alpha_A}{\alpha_B}-1\right)^2\right] > 0$$

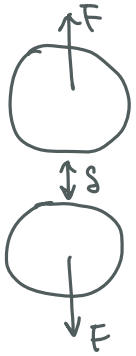
In a mixture, attraction between similar molecules is energetically more favourable than between dissimilar molecules. - The reason why the separation of two liquids by an interface into two phases can often be observed!

Dispersion forces prevail over orientation / induction forces, except for VERY polarized molecules.

Non-retarted, additive : $U(r) = -\frac{C}{r^6}$ unit: $10^{-76}\ J m^6$

	Debye	Keesom	Dispersion / London	Disp. Contribution
Ne – He	0	0	4	100%
HCL – HCL	6	11	106	86%
HI – HI	2	0.2	370	99%
$NH_3 - NH_3$	10	38	63	56%
$H_2O - H_2O$	10	96	33	24%

- Retarded rdW forces (macroscopic theroy by Dzyaloshinski, Lifshitz & Pitaevskii 1961)

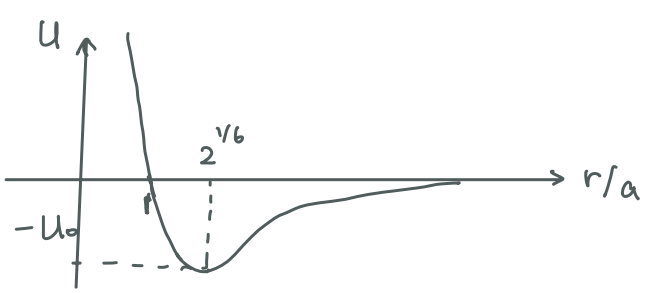


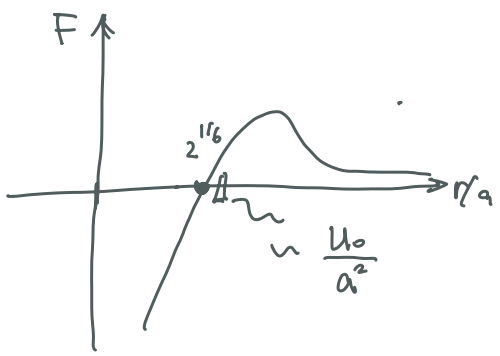
A correction of $\frac{1}{r}$ to account for the time effect on the interaction over long distances

$$U = \begin{cases} -\frac{C}{r^6} & r < 50\ nm \\ -\frac{C_{12}}{r^7} & r > 500\ nm \end{cases}$$

- Lennard – Jones Potential.

Quantum mechanics leads to an energy of repulsion related to $\exp(r_0/r)$ as r goes to 0. For mathematical convenience, it is written as $1/r^n$ with $n \geq 10$.



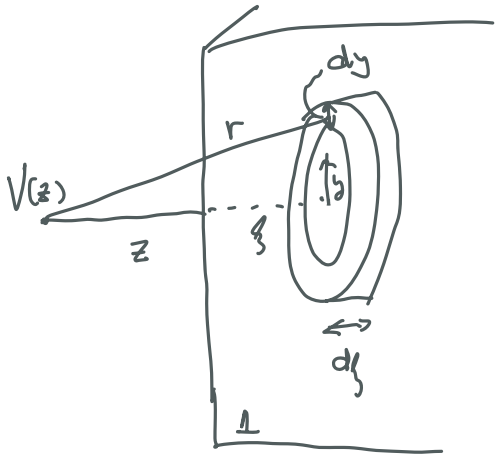


Born repulsion (empirical)

$$U = \frac{D}{r^{12}} - \frac{C}{r^6} = 4U_0\left[\left(\frac{a}{r}\right)^{12} - \left(\frac{a}{r}\right)^6\right]$$

VdW attraction between two surfaces

Assuming that vdw forces are additive (non-retarded). de Boer (1936) Hamaker (1937)



$w(r) = -\frac{C_{12}}{r^6}$ for m-m interaction

Interaction between a molecule and solid 1

$$V_1(z) = \int_V w(r)\left(\frac{\text{Atoms}}{\text{Volume}}\right) dV$$

$$= \int_{\xi=0}^{\infty}\int_{y=0}^{\infty} -\frac{2\pi n_1 C_{12} y\, dy\, d\xi}{[(z+\xi)^2+y^2]^3}$$

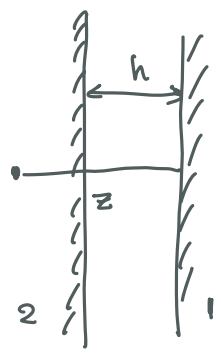
$r^2 = (z+\xi)^2 + y^2$

$\left(\frac{\text{Atoms}}{\text{Vol}}\right) = n_1 = \frac{\rho_1 N_A}{MW_1}$

$dV = 2\pi y\, dy\, d\xi$

$$= \int_{\xi=0}^{\infty} \frac{1}{2}\pi n_1 C_{12} \frac{1}{[(z+\xi)^2+y^2]^2}\Big|_0^{\infty} d\xi$$

$$= -\frac{1}{6}\pi n_1 C_{12} \frac{1}{(z+\xi)^3}\Big|_0^{\infty} = -\frac{\pi n_1 C}{6z^3}$$



$$V_{12} = \int_h^{\infty} -\frac{\pi n_1 C_{12}}{6z^3} n_2\, dz = +\frac{\pi n_1 n_2 C_{12}}{12 z^2}\Big|_h^{\infty} = -\frac{\pi n_1 n_2 C_{12}}{12 h^2}$$

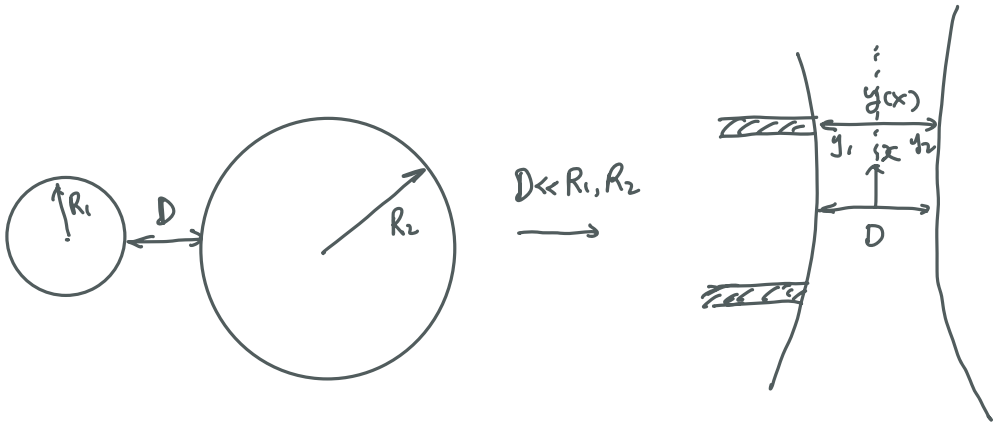
Interaction energy / unit area: $\boxed{V = -\frac{A_{12}}{12\pi h^2}}$ ← Hamaker constant

Interaction force / unit area: $\boxed{F = +\frac{dV}{dh} = \frac{+A_{12}}{6\pi h^3}}$ ← Attraction

$$A_{12} = \pi^2 n_1 n_2 C_{12} = \frac{\pi^2 N_0^2 \rho_1 \rho_2 C_{12}}{(M w_1)(M w_2)} \sim O(10^{-19} - 10^{-20}\ J).$$

$h \sim 0.3\ nm \rightarrow V \sim -30\ mJ/m^2$, $F \sim 100\ MPa$.

VdW attraction between two spheres (Derjaguin approximation)



$$F(D) = \int_0^\infty f(y)\, 2\pi x\, dx = \int_0^\infty \frac{A_{12}}{6\pi y^3} 2\pi x\, dx$$ (Attractive force)

(Force/area between two surfaces)

What are y_1, y_2?

$$\left[y_1 - \left(\frac{D}{2} + R_1\right)\right]^2 + x^2 = R_1^2 \Rightarrow y_1 = -\sqrt{R_1^2 - x^2} + \frac{D}{2} + R_1$$

$$R_1\sqrt{1 - \frac{x^2}{R_1^2}} \simeq R_1\left(1 - \frac{1}{2}\frac{x^2}{R_1^2}\right)$$

$$\simeq \frac{D}{2} + \frac{1}{2}\frac{x^2}{R}$$

Or $\nabla^2 y = K = \frac{1}{R} \rightarrow y_1 = \frac{D}{2} + \frac{1}{2R_1}x^2$

$$\rightarrow y_2 = \frac{D}{2} + \frac{1}{2R_2}x^2$$

- Accurate for $x \ll R_1, R_2$
- Breakdown when $x \sim R_1, R_2$. An correction expected scaling as $F_c \sim \frac{A}{R^3} \times R^2 = \frac{A}{R}$

$$\Rightarrow y(x) = D + \frac{1}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right)x^2 \rightarrow dy = \left(\frac{1}{R_1} + \frac{1}{R_2}\right)x\, dx$$

Therefore. $F(D) = \int_0^\infty \frac{A_{12}}{6\pi y^3} 2\pi \frac{R_1 R_2}{R_1+R_2} dy = \left(\frac{R_1 R_2}{R_1+R_2}\right) \frac{A_{12}}{6D^2}$

$$W(D) = -\left(\frac{R_1 R_2}{R_1+R_2}\right) \frac{A_{12}}{6D}$$

Note that ① $F_{sphere-wall} = \frac{RA_{12}}{6D^2}$, $W_{sphere-wall} = -\frac{A_{12}R}{6D}$

② Retarded interaction between a sphere and a wall

$$F(D) \propto \begin{cases} \frac{R}{D^2} & (\text{Non-retarded, small } D) \\ \frac{R}{D^3} & (\text{retarded, large } D). \end{cases}$$

③ 3 substances by Lifshitz (1956), Dzyaloshinski. Lifshitz. Pitaevski (1961)

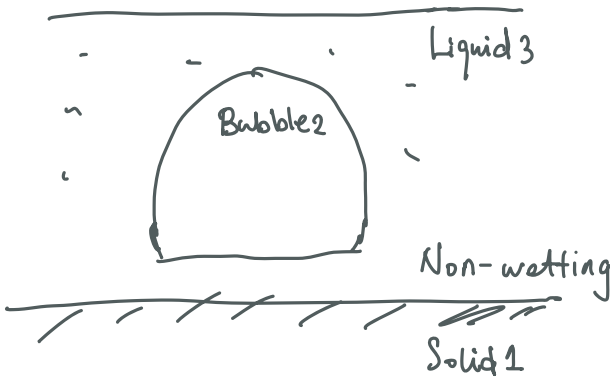
$$F(D) = \begin{cases} \frac{A_{132}}{6\pi D^3}, & \text{Small } D \\ \frac{B_{132}}{D^4}, & \text{Large } D \end{cases}$$

1 and 2 cross 3

$$A_{132} = \frac{3\hbar\bar{\omega}}{4\pi}, \quad \bar{\omega} = \int_0^\infty \left[\frac{\varepsilon_1(i\xi) - \varepsilon_3(i\xi)}{\varepsilon_1(i\xi) + \varepsilon_3(i\xi)}\right]\left[\frac{\varepsilon_2(i\xi) - \varepsilon_3(i\xi)}{\varepsilon_2(i\xi) + \varepsilon_3(i\xi)}\right] d\xi$$

↑ Dielectric permittivity

$$B_{132} = \frac{\pi^2 \hbar c}{240} \frac{1}{\sqrt{\varepsilon_{30}}} \left(\frac{\varepsilon_{10} - \varepsilon_{\infty 0}}{\varepsilon_{10} - \varepsilon_{30}}\right)\left(\frac{\varepsilon_{\infty 0} - \varepsilon_{30}}{\varepsilon_{\infty 0} + \varepsilon_{30}}\right) \varphi(\varepsilon_{10}, \varepsilon_{\infty 0}, \varepsilon_{30})$$

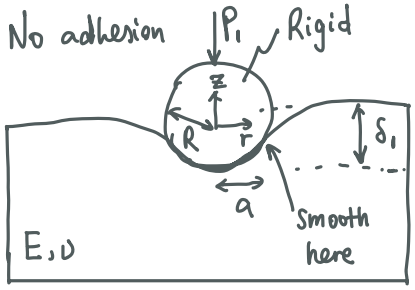


$A_{132} > 0$. Liquid does not wet.

$A_{132} < 0$, Liquid completely wets

Resisting adhesion

We have discussed JKR adhesion. The key idea in JKR (1971) actually is as follows

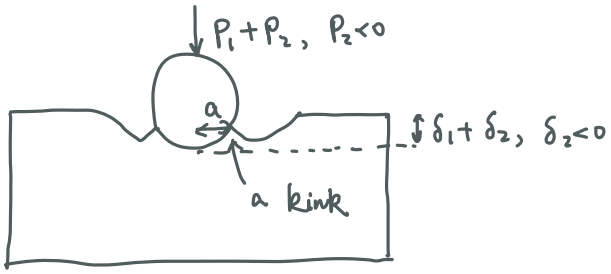


The solution to this bvp is

$$p_1(r) = \frac{2E^* \sqrt{a^2 - r^2}}{\pi R}, \quad P_1 = \frac{4E^* a^3}{3R}, \quad \delta_1 = \frac{a^2}{R}$$

($E^* = \frac{E}{1-\upsilon^2}$)

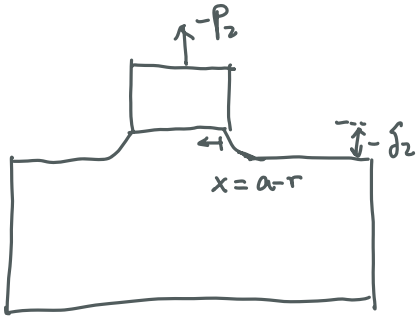
What if there is adhesion? Think of returning some P and δ.



Need to calculate P_1 and its consequences?

Note that the contact radius is maintained!!!

This means you can pull the sphere back a little bit (causing a uniform upward displacement δ_2 in the contacted area). Note that the systems are superposable b/c a is fixed. This pulling-back is exactly a flat rigid cylindrical punch problem.



The solution to this bvp is

$$p_2(r) = \frac{P_2}{2\pi a \sqrt{a^2 - r^2}}, \quad \delta_2 = \frac{P_2}{2E^* a}$$

The superposed P_2 is not arbitrary. The stress intensity cause by P_2 near the corner

is given by

$$p_2 = \frac{P_2}{2\pi a\sqrt{x(2a-x)}} = \frac{P_2}{2\pi a\sqrt{2ax}} \quad \text{as } x \to 0.$$

The related energy relase rate can be computed

$$K_I = \lim_{x\to 0} p_2\sqrt{2\pi x} = \frac{P_2}{2\sqrt{\pi a^3}}$$

$$G = \frac{K_I^2}{2E^*} = \frac{P_2^2}{8\pi E^* a^3} = \Delta\gamma$$

$$\rightarrow \quad P_2 = -\sqrt{8\pi E^* a^3 \Delta\gamma}, \quad p_2(r) = -\sqrt{\frac{2E^* a\,\Delta\gamma}{\pi(a^2-r^2)}}, \quad \delta_2 = -\sqrt{\frac{2\pi a\,\Delta\gamma}{E^*}}$$

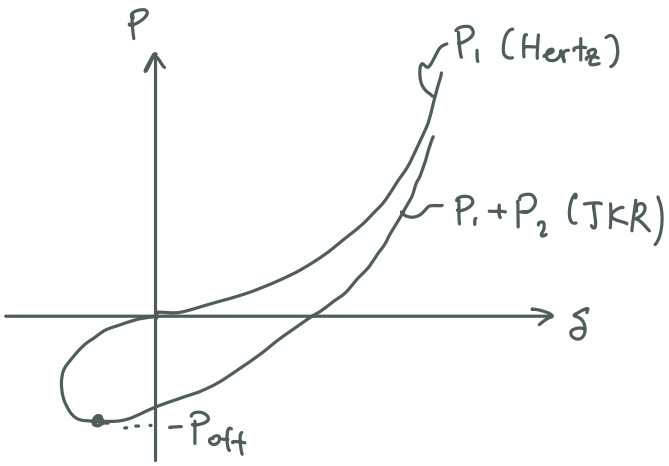
The solution to the adhesive contact between a rigid sphere and an elastic half space is then

$$p(r) = p_1(r) + p_2(r) = \frac{2E^*\sqrt{a^2-r^2}}{\pi R} - \sqrt{\frac{2E^* a\,\Delta\gamma}{\pi(a^2-r^2)}}$$

$$P = P_1 + P_2 = \frac{4E^* a^3}{3R} - \sqrt{8\pi E^* a^3 \Delta\gamma}$$

$$\delta = \delta_1 + \delta_2 = \frac{a^2}{R} - \sqrt{\frac{2\pi a\,\Delta\gamma}{E^*}}$$

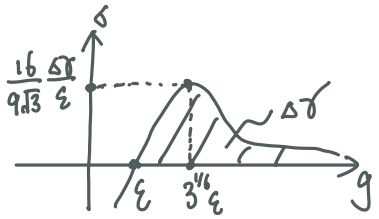
$$\rightarrow \quad P_{off} = \frac{3}{2}\pi R\,\Delta\gamma$$



P_{off} is independent of E^*!!! However, back to 1932, Bradley showed that

$$P_{off} = 2\pi\Delta\gamma R$$

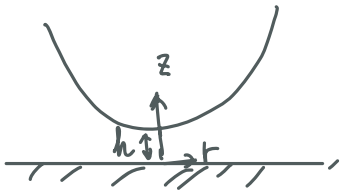
for separating a rigid sphere from a rigid surface.



$$\delta(g) = \frac{8\Delta\gamma}{3\varepsilon}\left(\frac{\varepsilon^3}{g^3} - \frac{\varepsilon^9}{g^9}\right)$$

vdW forces between the two surfaces of gap g

Suppose a rigid sphere of radius $R \gg \varepsilon$ is placed near a rigid half-space such that the point of closet approach corresponds to $g = h$.



$$g = h + \frac{r^2}{2R}$$

The interaction force is now:

$$F = 2\pi \int_0^\infty r\,dr\, \delta(g)$$

Since $dg = r\,dr/R$, we re-write

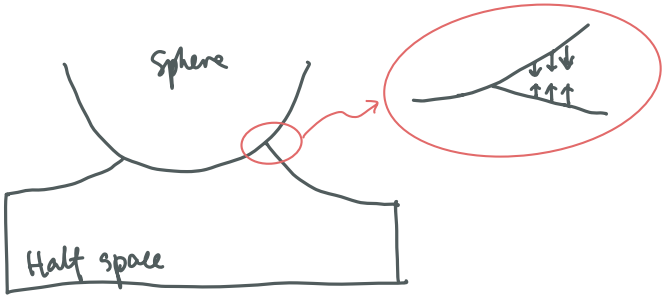
$$F = 2\pi R \underbrace{\int_h^\infty \delta(g)\,dg}_{\text{Energy}'} = 2\pi R \times \frac{\delta\gamma}{3\varepsilon}\left(\frac{\varepsilon^3}{2h^2} - \frac{\varepsilon^9}{8h^8}\right) = 2\pi R\,\delta\gamma\left[\frac{4}{3}\left(\frac{\varepsilon}{h}\right)^2 - \frac{1}{3}\left(\frac{\varepsilon}{h}\right)^8\right]$$

It is obvious that when $h = \varepsilon$, the force is maximized

$$P_{off} = 2\pi R\,\Delta\gamma$$

This conclusion applies for any contact problem with initial gap $g_0(r,\theta) = r^2 f(\theta)$.

Why $P_{off}^{JKR}\big|_{E^*\to\infty} < P_{off}^{Bradley}$? The interaction between bodies outside the contact area is not considered in JKR. Or the SSY condition is not satisfied in the rigid limit.

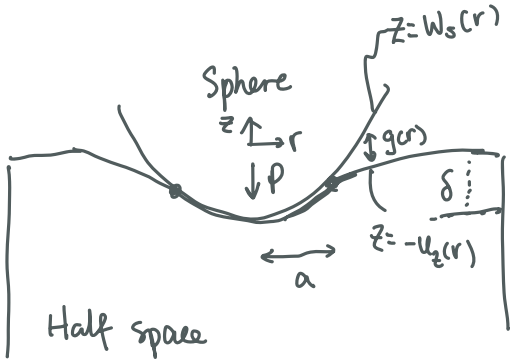


Several theories to bridge JKR and Bradley:

- Derjaguin et at. (1975) DMT theory
- Maugis (1992) Maugis - Dugdale theory
- Greenwood (1997) "Self-consistent model"

• DMT theory (A farewell?)

It essentially combines Hertzian contact solution (no adhesion) and δ-g law.



Assuming Hertzian contact so that

$$u_z(r) = \frac{(2a^2-r^2)}{\pi R}\,\mathrm{Arcsin}\left(\frac{a}{r}\right) + \frac{a\sqrt{r^2-a^2}}{\pi R}, \quad r>a$$

($u_z(r)$: downward displacement)

The adhesive fore is computed in the region outside the contact:

$$F_1 = 2\pi\int_a^\infty \sigma(g)\, r\, dr, \quad g = \xi + \frac{r^2}{2R} - \delta + u_z(r)$$

(ξ: equilibrium.)

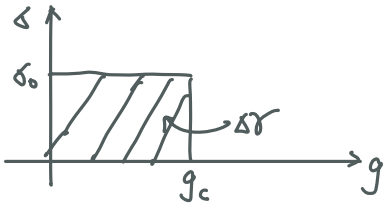
So the total indenting force is $P = P_H - F_1$

(P_H: Hertz; minus for attractive adhesion.)

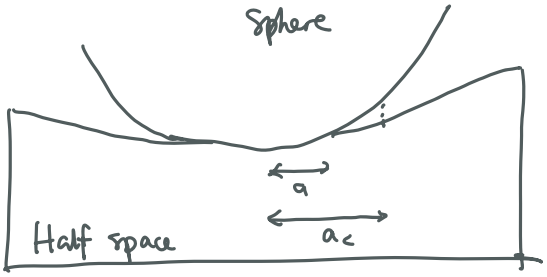
The DMT theory is rough, particularly in the consideration of elastic deformation in both $[0,a]$ and $[a,\infty)$. However, somehow it predicts the same pull off force as Bradley.

• Maugis' solution

Maugis (1992) made the further simplification of using a Dugdale cohesive zone approximation (Dugdale, 1960) and solved the bvp with mixed boundaries.



Dugdale cohesive law.

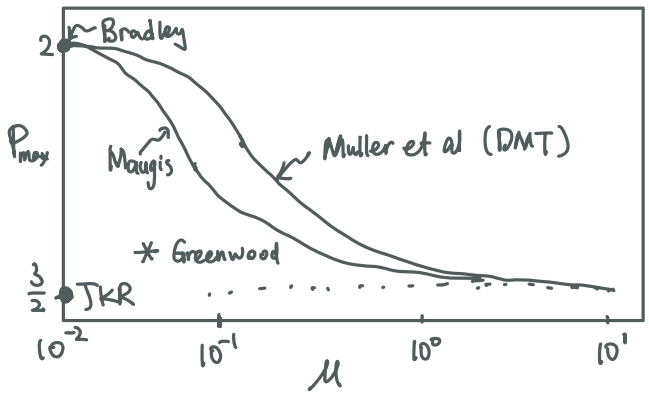


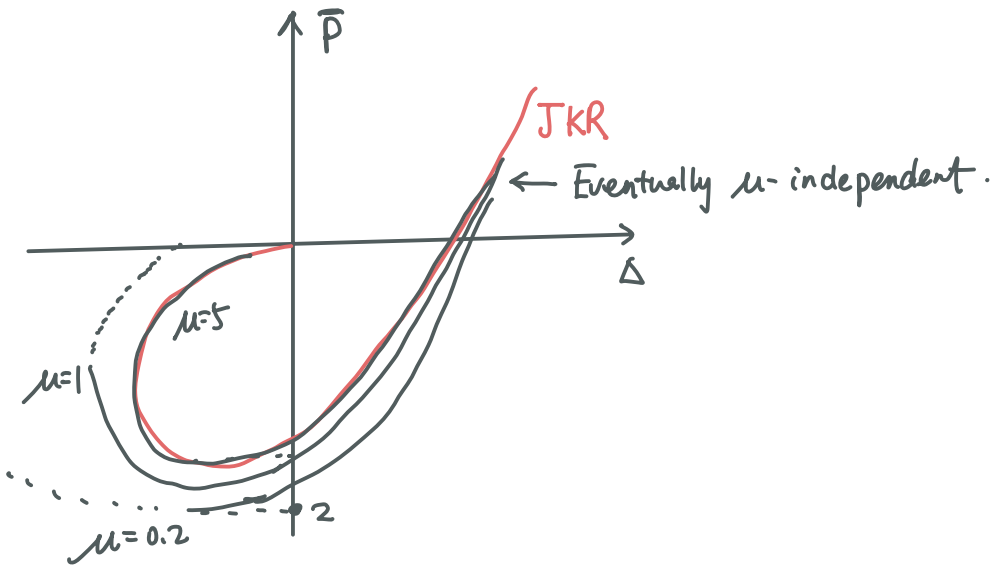
- $0 < r < a$, prescribed displacement (by the indenter)
- $a < r < a_c$ (?), $\sigma_{zz} = +\sigma_0$ (at $r = a_c$, $g = g_c$)
- $r > a_c$, $\sigma_{zz} = 0$

An important parameter arises here defined by Tabor

$$\mu = \left(\frac{R \Delta\gamma^2}{E^{*2} \varepsilon^3} \right)^{1/3}$$

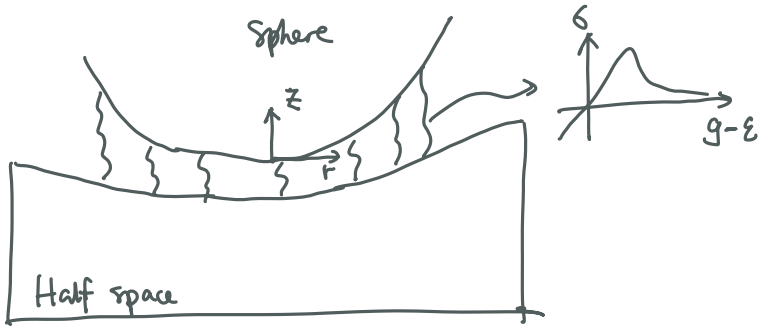
(to be discussed soon).

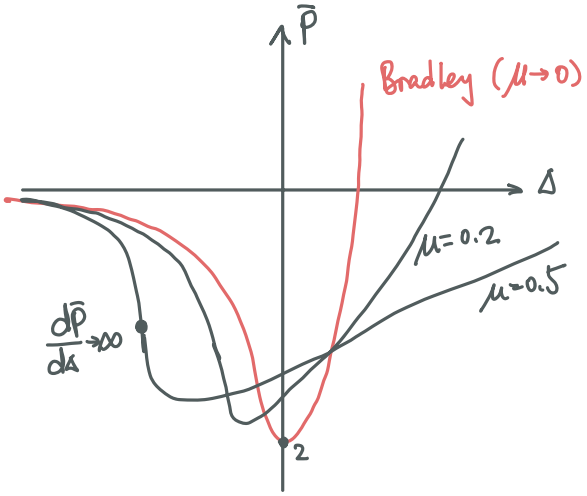


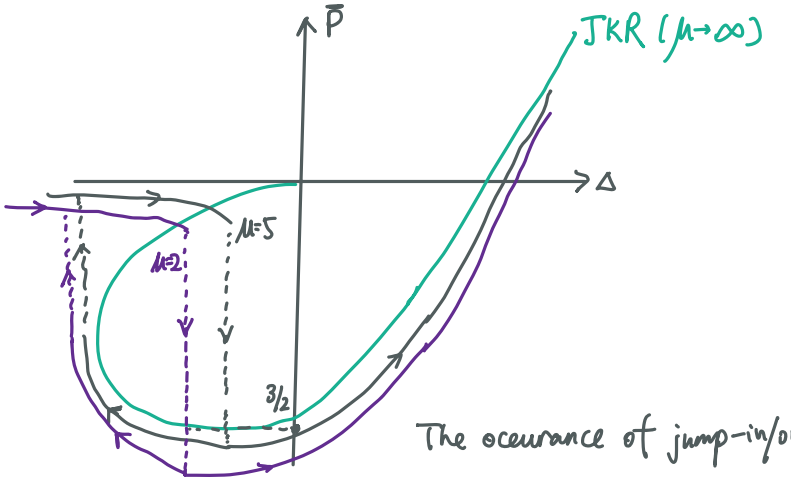


- Greenwood's solution

Greenwood (1997) directly solve the bvp with the consideration of long-range intermolecular forces.

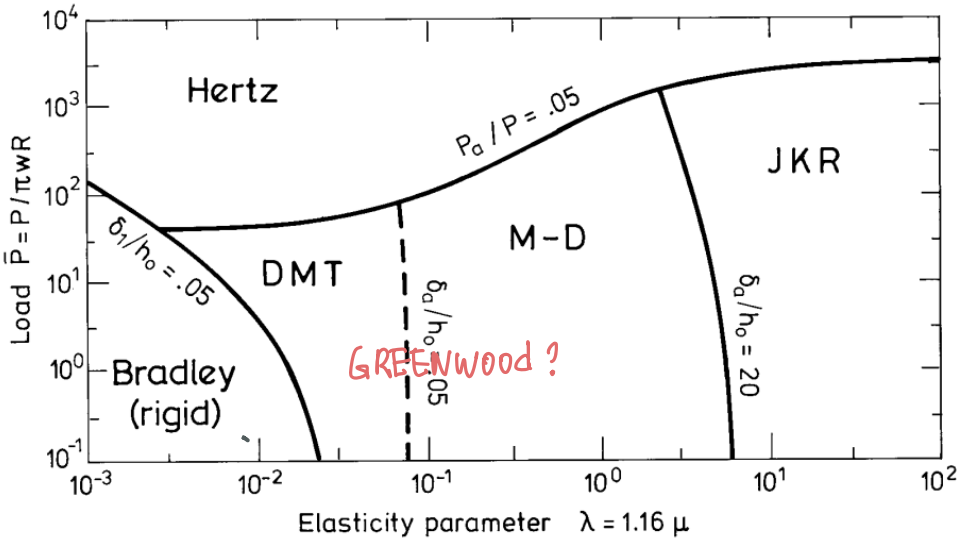






The occurance of jump-in/out!!

Let us make a summary here via an adhesion map drawn by Greenwood and Johnson (1997).



Finally how to understand the Tabor parameter (1977) that can be used to bridge different models or to know whether small-scale δ-g laws to be considered?

- Point of view of vertical lengths. Recall we used $\delta_* := \left(\frac{\Delta\gamma^2 R}{E^{*2}}\right)^{1/3}$ to define rescaled vertical displacement in JKR. Natural to have a micro parameter by taking $\delta_{\text{micro}} = \varepsilon$.

$$\mu = \frac{\delta_*}{\delta_{micro}} = \left(\frac{R\Delta\gamma}{E^{*2}\varepsilon^3}\right)^{1/3} \quad \text{so that} \begin{cases} \mu \gg 1 \rightarrow \Delta_{\delta=\varepsilon} \ll 1 \\ \mu \ll 1 \rightarrow \Delta_{\delta=\varepsilon} \gg 1 \\ \text{Regime of interet } \Delta \sim 1 \end{cases}$$

- Point of view of horizontal lengths. Again from JKR theory, we have $a_* := \left(\frac{\Delta\gamma R^2}{E^*}\right)^{1/3}$ for rescaling ($\delta_* / a_*^2 \sim R$). We want to use this to compare to a microscale horizontal lengthscale to obtain μ.

Note that the stress field near the contact line is given as

$$\sigma \sim \frac{K_I}{\sqrt{2\pi r}} \sim \sqrt{\frac{E^*\Delta\gamma}{\pi r}}.$$

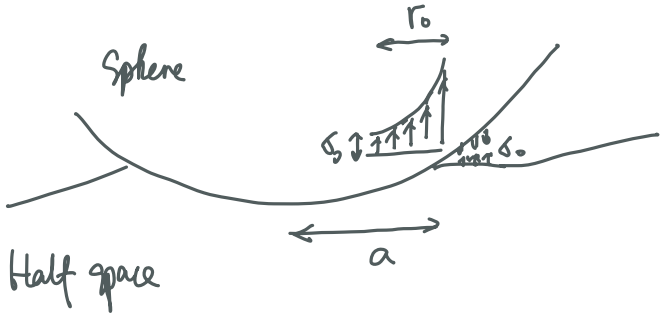
JKR did not consider the adhesive interactions outside the contact area in which $\sigma \sim \frac{\Delta\gamma}{\varepsilon}$. An natural horizontal length (in the contact area) appears:

$$\sqrt{\frac{E^*\Delta\gamma}{\pi r_0}} \sim \frac{\Delta\gamma}{\varepsilon} \rightarrow r_0 \sim \frac{E^*}{\Delta\gamma}\varepsilon^2$$

It can be shown that

$$\frac{a}{r_0} = \left(\frac{R\Delta\gamma^2}{E^{*2}\varepsilon^3}\right)^{2/3} = \mu^2$$

Physical picture:



$\mu \gg 1 \rightarrow a \gg r_0$

$\mu \ll 1 \rightarrow a \ll r_0$